

THERMOELECTRIC MODULE AND GENERATOR

The invention regards a module for thermoelectric applications and a generator of electric power formed with a plurality of such modules.

It is well known in the art the use of the thermoelectric properties of some materials for generating electric power by means of the Seebeck effect or for cooling electronic components by means of the opposed effect, i.e. the Peltier effect.

For sake of brevity, in this description and in the appended claims reference will be made mainly, where not otherwise specified, to the electric power generation with Seebeck effect; however, what will be stated shall not be intended in a limiting manner and the issues set forth must be considered valid, *mutatis mutandis*, also for the cooling of electronic components or other utilisations based on the Peltier effect. There are many technological and scientific publications on this subject to which reference should be made for further information, whereas for sake of clarity in this connection it is worth considering herein US Patent No. 6,274,802 (Fukuda et al.) and US Patent application No. US2002/0046762 in the name of the same applicant of the present application.

The Fukuda patent discloses a synthesized semiconductor for thermoelectric devices, obtained following to the hot compression of powders of bismuth (Bi), tellurium (Te), selenium (Se), and antimony (Sb).

The semiconductor material so obtained is useful to make thermoelectric components of opposed polarity (positive and negative), which are connected in series (and/or in parallel) by means of metallic straps.

The patent application to Rossi claims a module made by a thermoelectric couple built up with oriented crystal structures of bismuth and tellurium salts, doped with selenium for the negative pole and with antimony for the positive pole.

The thermoelectric poles of each module are connected by conductive metallic straps likewise in the previous case.

In these two prior documents, the thermoelectric components have the shape of a parallelepiped with a thickness greater than 1 mm; this generates an ohmic resistance which in both cases is faced by providing oriented crystals of the semiconductor materials, but which cannot be reduced below certain limits, also taking into account the resistance due to the contacts between the semiconductors and the straps

connecting the modules of the generator.

Indeed these straps are made of a different material from the thermoelectric elements, so that the discontinuity occurring at their junction determines an additional ohmic resistance.

It is an object of the present invention to improve this state of the art. Namely, it aims at providing a thermoelectric module comprising a pair of semiconductor elements of opposed polarities coupled by conducting metal straps, having such structural and functional features as to obtain improved performance comparing to known modules, either as regards the tension generated and to the lower ohmic resistance involved.

This object is achieved by a module characterized in that one of the conductive metal straps has a portion coated with a first thermoelectric material, and another portion coated with a second thermoelectric material of polarity opposed to the first one.

The layers coated upon the strap have a thickness less than 1 μm (0,001 millimeters) and preferably in the order of 0,1 μm (0,0001 millimeters); among the materials used for the thermoelectric layers there are the couples platinum-selenium and aluminum-selenium, but the preferred couple is platinum-tellurium, while the conductive strap are made of copper, aluminum or other good electric conductor.

The module so obtained can be piled up or connected in series with other similar modules by means of further conductive straps, thereby forming an electric power generator.

These and further characterising features of the invention will result better from the description set forth hereafter, regarding a preferred but not exclusive embodiment thereof, shown in the drawings enclosed wherein:

- fig. 1 shows a strap coated with thermoelectric materials, according to the invention;
- fig. 2 shows thermoelectric modules according to the invention, connected in series;
- fig. 3 shows thermoelectric modules like those in fig. 2, with the upper and lower faces respectively cooled and heated;
- fig. 4 shows a generator made by thermoelectric modules according to the invention, in an stacked configuration;

- fig. 5 is a diagram showing the tension variations in function of the temperature, obtained with thermoelectric modules according to the invention.

In the first of these figures numeral 1 indicates a copper strap shaped as a parallelepiped, 20 mm long, 10 mm, wide and 7 mm thick.

Half of the upper face of the strap 1 is coated with a layer of platinum 2, while the other half is coated with a layer of tellurium 3; such layers, which have a thickness less than 1 μm and preferably of 0,1 μm , are obtained from evaporation in a high vacuum environment of respective the metals having 99,99% purity rate.

Nevertheless, any other technology (e.g. sputtering) suitable for applying similar layers of Pt or Te may be used.

The thermoelectric module including the strap 4 with the layers 2, 3, is completed by another copper strap 4 (fig. 2, 3) equal to the first one, but without coating layers.

For providing the serial connection of thermoelectric modules according to the invention, the second strap 4 is put upon the first one in a staggered condition, as shown in fig. 2, covering one of the two layers 2 and 3; the straps 1 and 4 are then kept together by means of springs 7.

Obviously springs can be replaced by other means (for instance bands) suitable to hold together the straps firmly for achieving a good electrical contact between the juxtaposed surfaces, without damaging the thin layers 2 and 3.

If is for this reason that mechanical systems are preferred for fastening the straps than those based on weldings, which can damage the aforesaid layers because of the high temperatures involved.

To generate electric power, the thermoelectric modules connected in series have the two faces put at different temperatures; so, for example, in fig. 2 the inferior faces of the straps 1 are cooled by a liquid flowing in a hollow space 10, adjacent to them.

Generally, the hot face of the modules should be at a temperature higher than 35- 40 °C, while the cold face should be at less of about 15- 20 °C.

Of course the difference in temperature between the faces of the modules may be larger than this and obtained with many other solutions, depending on the different uses of the present invention and of the electric power to be generated.

For example it will be possible to take advantage of the waste heat released from hot walls such as those of furnaces, internal combustion engines or others, and of those

heated by the sun (reference could be made to solar panels or similar); as an alternative, the heat may be supplied by flames or electric heaters and the like.

Another possible constructive solution is shown in fig. 3, wherein the upper face of the modules is cooled by the coil 13 of the vaporizers of a refrigerating apparatus, while the other face is heated by the condenser 14 of the same apparatus.

This solution makes it possible to recover energy from a motor intended for other purposes, e.g. for automotive use, which drives the compressor of the refrigerating apparatus by means of a transmission belt or similar.

From the functioning point of view, the thermoelectric module of this invention allows the generation of electric power (by Seebeck effect) or the cooling of electronic components (by Peltier effect) with a much higher efficiency than in the state of the art.

Indeed, the ultra thin layers 2,3 of the thermocouples reduce by orders of magnitude their ohmic resistance; this effect is further enhanced by the wide surface, versus the thickness, of the layers.

Furthermore, the latter are applied upon the substratum formed by the strap, 1 in a way which allows a close junction therewith, thereby eliminating any contact ohmic resistances due to discontinuity.

On this subject it is worth to underline that in the prior references considered above, it is not explained how the elements of the thermocouples are fixed to the straps; nevertheless, if such fixing were obtained by means of welding, the melted region of the thermoelectric material would be somehow physically altered (reference should be made here to the fact that in both documents cited, the orientation of the crystals in thermoelectric couples is critical).

Last it is important to add that unexpected good results have been reached with modules wherein the material for one of the thermoelectric layers is platinum, particularly when it is used in combination with tellurium for the other layer.

Indeed this couple has proved to maintain a high performance stability in the time.

The efficiency of the thermocouple platinum- tellurium is shown in the diagram 5, reporting the yield (in millivolts) in function of the difference of temperature between the hot and the cold faces of ten thermoelectric modules, with straps having the same dimensions of that of the strap in fig. 1, connected in series as explained

above.

In this respect it is important to emphasize that even if the platinum is very expensive, the use of ultra thin layers as above described, makes economically competitive the industrial application of this invention.

Of course, the latter may be subject to variations with respect to the embodiment herein considered.

First of all it should be pointed out that although there have been shown modules with flat shape (the straps 3,4 are parallelepiped), they could also be made with a cylindrical geometry; reference should be made to the case of modules connected in series, as seen before, but with a circular layout applied upon a cylindrical surface like, for example, that of a hot pipe, for generating power exploiting the heat of fumes or of another fluid flowing therein, which would be otherwise wasted.

This result has been rendered possible by the ultra thin thermoelectric layers, which can be applied even upon non-flat substrata contrarily to what occurs for the semiconductors of parallelepiped shape of the prior art.

In other words the use of layers of 1 μm or less allows the efficient application (by means of vacuum vaporization, sputtering or other), of thermoelectric materials even upon surfaces not flat, without obstacle or loss of efficiency.

Also for what it concerns the thermoelectric materials there can be changes with respect to the couple platinum-tellurium: for example among the couples which gave good yield mention can be made to platinum-selenium, selenium aluminum, and alloys nickel/ chrome alloys (doped with C,Si,Fe)- nickel/copper alloys (doped with C,Si,Mn,Cr,Fe,S).

The following tables 1, 2, 3 report the voltages obtained with 10 modules as described above, utilizing different couples of thermoelectric materials (the p between brackets indicates the positive pole, whereas n stands for the negative one).

In the tables the first two columns indicate respectively the temperature in $^{\circ}\text{C}$ of the cold and of the hot side of the modules, while the third and fourth columns report the voltage (in mV) measured respectively for modules connected in series as in fig. 2, and modules stacked as it will be better described later.

Table 1

Couple Platinum (p)-Tellurium (n)

Temperature	Temperature	Voltage	Voltage
Cold side	Hot side	Modules in series	Modules stacked
20	30	5	2
20	40	10	4
20	50	16	7
20	60	21	10
20	70	26	12
20	80	32	15
20	90	37	18
20	100	42	20

Table 2

Couple Selenium (p)-Aluminium (n)

Temperature	Temperature	Voltage	Voltage
Cold side	Hot side	Modules in series	Modules stacked
20	30	6	2
20	40	12	5
20	50	18	8
20	60	22	10
20	70	28	13
20	80	33	16
20	90	39	19
20	100	45	22

Table 3

Couple NiCr alloy (p, doped with C, Si, Fe) – NiCu alloy (n, doped with C, Si, Mn, Cr, Fe, S)

Temperature	Temperature	Voltage	Voltage
Cold side	Hot side	Modules in series	Modules stacked
20	30	2	1
20	40	4	2
20	50	8	3
20	60	11	4
20	70	14	6
20	80	17	8
20	90	20	9
20	100	22	10

Turning now to consider the piles of thermoelectric modules, reference should be made to fig. 4 wherein it is shown a generator 20 made by stacks of straps 1 coated with the layers 2,3 according to the embodiment of fig. 1; in the piles the straps 4 without thermoelectric layers are not present anymore and the connection between the modules is provided by the coated straps 1.

As it can be seen, according to this embodiment the straps are offset thereby protruding from the edge; this allows to form a temperature difference between the upper and the lower faces, for example by convection utilising cold or hot air jets, or by means of one of the cooling (or heating) system described above.

For example it could be envisaged to place the coils of the evaporator and of the condenser of a refrigerating apparatus, on the surfaces of straps 1 protruding from the sides of the generator in fig. 4.

The protruding ends of the straps can be insulated from each other in a known manner, for instance by means of ceramic material or silicon oxide (SIO).

The piles of straps 1 rest upon a bar 22 of copper and a similar bar 23 is put at their upper end.

The generator 20 includes an outer supporting structure 25 having the shape of a frame and made with insulating material (such as plastics or others); in the upper part of this structure there are screwed shanks 27 which, once they are screwed, press the

piles of thermoelectric straps urging on the upper bar 23.

With this embodiment of the invention there have been obtained good results and for sake of brevity, reference can be made to the explanations given before.

It just matters to be pointed out that equivalent generators can be obtained by increasing the number of piles arranged side by side, or also by using only one pile.

Moreover, it is possible to make generators wherein the straps are stacked in regular manner one upon the other (i.e. not offset), and further ones which make use of heating or cooling means arranged upon and under the piles instead of the copper bars 22, 23, which in these cases would be placed along the sides of the piles.

Last, it must be recalled what has been set forth at the beginning about the fact that the thermoelectric modules of this invention are useful also for cooling electronic components or for other applications based on the Peltier effect, besides the power generation.

All of these alternatives are encompassed by the scope of the following claims.